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Development and mechanical properties of carbon fibre reinforced EP/VE hybrid composite systems

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RESEARCH ARTICLE

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Abstract

In this study epoxy/vinyl ester (EP/VE) based hybrid thermoset resin was developed and used as a matrix in unidirectional carbon fabric reinforced composite. The mechanical characteristics of the hybrid and the individual resins were revealed by dynamic mechanical analysis (DMA), three-point bending, and hardness tests. The produced composites were investigated by three point bending, impact-, and fatigue tests. The morphological characterization of the materials was carried out by atomic force microscopy (AFM). The revealed morphology affirmed that the mechanical properties of the composites were improved by the using of the hybrid resin. Based on the results enhanced inter-laminar properties of the produced composites were exhibited.

Keywords

Hybrid resin · fatigue · composite · epoxy · vinyl ester · IPN

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Introduction

In the field of thermoset polymer composites the researchers work on materials and their combinations which give more favourable mechanical properties. The thermoset structural composites have great strength and modulus, but their toughness properties are often worse than that of ductile metals and alloys or thermoplastic matrix polymer composites. These high performance materials usually give rigid reactions to quickly forthcoming actions, loadings. The solution for toughening can be found in the micro-, or nano-scale structure of the thermoset polymer. In the fibre reinforced composites usually the matrix is responsible for the toughness, therefore mainly the matrix should be modified to improve of this property [1, 2].

Basically, there are two different ways to create micro-, or nano-structure in the polymers. The first opportunity is the hybridization of the reinforcing materials with micro or nano sized particles. Nowadays this technique is quite popular among researchers and manufacturers, because of the easy reproducibility of these composites. The effectiveness of this third phase is based on the properties of the particle itself and on the surface to volume ratio that has main role in the quality of the adhesion. The specific surface can be extremely huge in case of nanoparticles. Another way to achieve micro- or nanostructured systems is to change the matrix morphology by blending. In this approach researchers try to make a mixture of different polymers, which are well distributed in each other and the border area of their phases (interphases) has large surface, where a lot of secondary bounds are present. One example of such structure is the interpenetrating polymer network (IPN) system, in which the different polymer phases are not separated, but the polymer chains penetrates into the other cross-linked structure of the other phase. In these systems a sort of synergistic effects there can be found. Due to this fact the IPN structure can absorb remarkable amount of energy by their flexible properties. This feature can be manifested in mechanical, thermal and thermo-mechanical properties too [1-3].

The mentioned synergistic effects and the compatibility of mixed polymers affect the thermo-mechanical properties.

Lipatov [3] was one of first researchers who dealt with the IPN systems and developed a method for define the segregation degree of the two component in the mixture. In this method the segregation degree (α) varies between zero and one. The zero segregation degree (α = 0) means, that the components are absolutely compatible with each other. If the segregation degree equals one (α = 1) means the absolute incompatibility.

The thermoset IPNs are among the best candidates for matrix material in fibre reinforced composite systems, because beside the improved static-mechanical properties, the toughness can also be enhanced by using these materials. There are basically two methods to produce IPN. First is the sequential formation, wherein the first step is the production of a crosslinked polymer then this polymer is swollen by the monomers or oligomers of another polymer. Finally the crosslinking of the second polymer is carried out. Another way is the simultaneous method, where the monomers of both polymers are mixed together and then their own cross-linkers are added to the system. For the appropriate structure it is prerequisite that the crosslinking mechanisms of the resins do not hamper each other. [3-5].

In the field of thermoset IPNs, the researchers have investigated a variety of material combinations like epoxy resins (EP) with polyurethanes (PU) [6-9], unsaturated polyester (UP) resins with PU [10, 11], EP with vinyl ester (VE) resins [4, 5, 13-15], and EP with UP resins [16, 17]. Most of the investigations focused on improving the mechanical behaviours. From the viewpoint of composites one of the most important properties is the toughness which can be characterized by fracture tests. For toughness characterization of IPN structured thermosets the linear elastic fracture mechanical approach has been well established [5].

The mixture of most commonly used (in aircraft industry and shipbuilding) EP and VE resins can give better mechanical properties and toughness than the individual components. In case of EP/VE resins the appropriate mixing ratio to get IPN structure is found to be around 1:1 [4].

Szabó et al. [18] worked with EP/VE systems as matrix with ceramic fibre mat reinforcement. They used different surface treatments on the mat for EP and VE resin components. They used aliphatic (Al) EP with cycloaliphatic (Cal) hardener. Their study paid a great attention for the impact of surface treatments on the mechanical behaviours.

Karger-Kocsis et al. [19] used Al and Cal EP resins. These resins were hardened with Al and Cal amines. They applied bisphenol A -based VE resin with 30% styrene content. In this study the dissipation factor (tan δ) was investigated at various mixtures and the molecular structures were studied with AFM. The results of the value of tan δ of the mixtures gave evidence that the formed structure is IPN.

As in case of IPNs the connection between the phases is on molecular level, it is hard to decide if the structure is really interpenetrated. For IPNs it is proved that the glass transition temperature (T_g) of the mixed resin (EP/VE) is between of the two individual resin ones, therefore it can be a clear sign for the proper structure [3-5, 19, 20].

Nowadays the field of hybrid resins is relatively well investigated [4-16, 21-23]. In case of hybrid matrix composites the researchers investigated mainly the molecular structure and the reinforcement-matrix connection [18, 24], the structure-mechanical relationship is less investigated. The aim of this study is the development and the characterization of mechanical advantages of epoxy/vinyl ester resin based carbon fibre reinforced composite system.

Materials

As matrix material EP and VE resins were used. The EP consisted of a bisphenol A diglycidyl ether EP resin (with 188 g/epoxy equivalent, 12000 mPa·s viscosity at 25°C, and 1.17 g/cm^3 densiy, Ipox ER 1010 product name, manufactured by Ipox Chemical Hungary) and isophorone diamine hardener (with 43 g/hydroxy equivalent, 5-25 mPa·s viscosity at 25°C, ~660 mg KOH/g amine value, Ipox EH 2293 product name, manufactured by Ipox Chemicals, Hungary).

The VE resin (bisphenol based, with 1300 mPa·s Brookfield viscosity 5 rpm at 25°C, 35% styrene content, AME 6000 T 35 (product name), manufactured by Ashland Italia S.p.A., Italy) with 2 wt% in diisobutyl phtalate dissolved methyl-ethyl ketone peroxide accelerator MEKP-LA-3 (product name), manufactured by Peroxide Chemicals, South Africa) were used.

As reinforcing material unidirectional Panex 35 FB UD 300 type carbon fabric was used (sized for epoxy, with 1,449 MPa tensile strength and 126 GPa tensile modulus, manufactured by Zoltek Zrt., Hungary).

Experimental

In the first step of the matrix preparation the 1:1 rate EP/VE resin mixture was stirred for ten minutes. Then the amine of EP was added in and stirred for two further minutes again. Finally the catalyst of VE was added also stirred for two minutes. For preparation of specimens (4x10 mm cross section) silicone moulds were applied. Composites were made by simple hand lay-up method using 6 unidirectional carbon fabric layers, the orientation of the layers was the same. After the hand lay-up the laminates were pressed between parallel steel plates by hydraulic press with 0.5 MPa compressive stress at 25°C temperature. Beside the EP/VE matrix, reference composites with exactly the same reinforcement orientation and content, were also prepared with EP and VE. The nominations of these composites are EP/VE/CF; EP/CF and VE/CF, respectively.

After 24 hours of crosslinking all of the moulded resins and laminated composites were cured at 80°C for 4 hours.

On the cured resin specimens dynamic mechanical thermal analysis (DMA) were performed with a Q800 (TA Instruments, New Castle, DE, USA) device in three point bending mode

(with 1 Hz load frequency, strain actuation, the average specimen size was 50 x 10 x 4 mm). The measuring temperature range was 20-150°C, the heating velocity was 2°C/min.

Shore D hardness was measured by Zwick Roell HO4 3150 type equipment according to ISO 868:2003 at room temperature. The average hardness was calculated by using of 20 different measuring point on the surface of one specimens.

Charpy-type impact tests were performed by a Ceast Resil Impactor impact testing machine (Italy) equipped with a 2 J impact energy hammer and a DAS 8000 data collector unit. The composites were tested according to ISO 179-2:2000. The nominal size of the specimens was 80 x 10 x 2 mm, they were hit by their cross-section along the face normal to the fibre direction. The orientation of the reinforcement was perpendicular directed to the face normal of the samples and they were embedded to longitudinal direction (parallel their largest, 80 mm length dimension).

The flexural properties were evaluated for resin sand composite specimens according to ISO 178:2003 and ISO 14125:1999, respectively. The flexural tests were carried out on a Zwick Z020 (Germany) universal testing machine. The test speed was 2 mm/min, the gauge length was 64 mm (with 10 x 4 mm cross section) for the resins and 80 mm (with 15 x 2 mm cross section) for the composites. In case of flexural tests of composites the method was longitudinal three point bending, because that way could give more information on the maximal reinforcing effect of the carbon fibres.

The fatigue properties of the composites were characterized by an Instron 8872 (USA) fatigue testing machine in flexural mode (with 100 x 15 x 2 mm size test specimens, 80 mm gauge length), according to the ISO 13003 standard. The test was carried out in force controlled mode, the load factor (Lf) was 0.95, the stress ratio (R) was 0.1 and the frequency of the loading was 5 Hz. The fatigue flexural tests of the composites was carried out in the specimens longitudinal direction embedded reinforcement. This way the quality of fibre/matrix connection could be shown by the fatigue test properly.

Selected resin specimens and composites were investigated by atomic force microscope. Before the AFM test the samples were carefully prepared and embedded in epoxy resin. Then the samples were polished by multi-phase method to reach on their surface the 1 μm average surface asperity. For this investigation was used Veeco/Digital Instruments Inc. (USA) Multi Mode AFM-2 machine, in tapping mode, the frequency of the needle was 364 Hz.

Results and discussion

First the DMA tests were carried out, Fig. 1 shows the tan δ as a function of the temperature. One can see, that the mixing was effective, as the T_g of the EP/VE is between the two pure matrix material ones. As the T_g of the mixture material can be calculated as an average of the two component ones, therefore

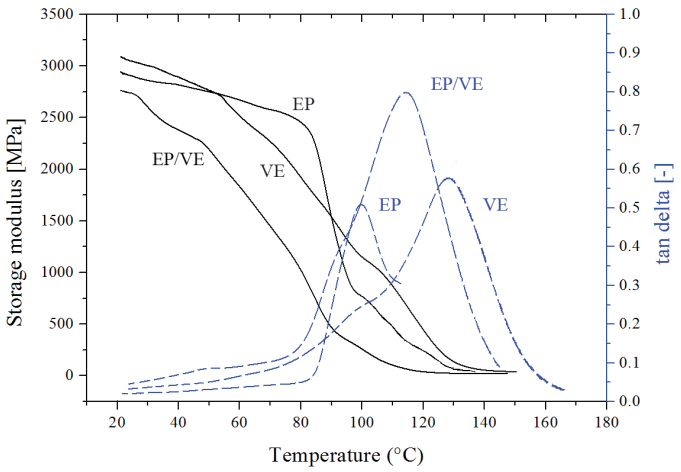

Fig. 1. The storage modulus - temperature and the tan δ - temperature curves of the mixed epoxy/vinyl ester resin and its components

it can be concluded that the compatibility of the resins is perfect. Overall the results refers that the simultaneous production form was successful and most probably IPN structured material was prepared. Between the EP and VE mainly secondary bonds are present but primary bonds also can be formed (between secondary hydroxyls in VE and oxirane groups of EP). The formation of this primary bounds need relative high activation energy from the curing or the heat generation of the polymerisation process. In this case it does not have great probability, because of the relatively low temperature curing and relatively small specimen thickness that results low heat generation in the material. The formed primary bonds can result an additional strengthening effect between the two phases.

The most important results of the DMA measurements are tabulated in Table 1. It is observable that the hybrid resin has much higher dissipation factor (tan δ) compared to the individual EP and VE resins. It may be related to the improving of the damping properties in the mechanical test. An important result is that around room temperature the EP/VE resin has locally the highest tan δ values of the investigated materials.

The storage modulus of the mixed resin is close to the EP and VE resins. The moderate decrement shows that the crosslinking mechanisms did not hamper each other that refers to the crosslinking density in the EP/VE mix was on a good level.

Tab. 1. The main results of DMA tests

Designation	EP	EP/VE	VE
T_g [°C]	100	114	129
tan δ_{max} [-]*	0.51	0.80	0.58
E' [MPa]**	2920	2790	3080

*at T_g; **at 20°C

The results of flexural test can give more information about the mechanical behaviour of the different resins. The three-point bending test of the resin-specimens showed that the mixed resin had higher flexural strength with lower standard deviation as related to the other two materials (Fig. 2). The reason of the increment can be explained by the structure of the material. The entanglements of the hybrid resin chains have greater potential of energy absorption, and can hamper the crack propagation in the material.

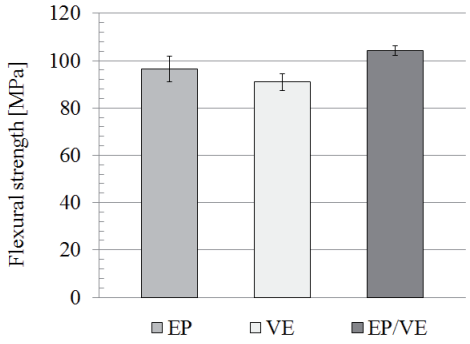

Fig. 2. Flexural strength of mixed resin and the individual resins

The Shore D hardness results (Fig. 3) affirms, that the crosslinking density in the EP/VE resin is in the appropriate range, because the hardness depends to the crosslinking degree and the mixed resin takes place between its components.

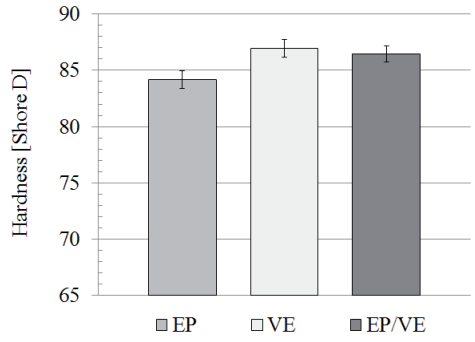

Fig. 3. Shore D hardness of the hybrid resin and its components

The most common loads in case of a fibre reinforced polymer composite are the flexural ones. The results of the flexural tests of the prepared composites showed that the mixed resin containing one has the highest flexural strength (Fig. 4). Based on the results of the resin tests this phenomenon is not surprising, and the explanation is also similar: because of the entanglemented structure the crack-propagation is hampered therefore the matrix material has greater role in the load distribution which leads to higher strength.

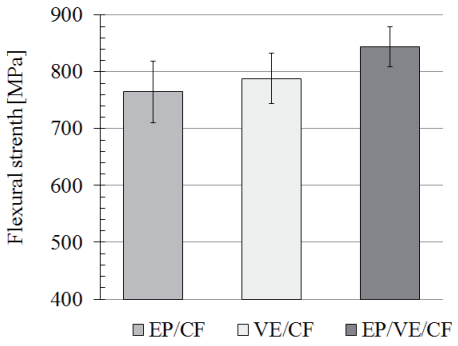

Fig. 4. Flexural strength of the investigated composites

The values of the flexural modulus are shown in the Fig. 5. It is noticeable that the average flexural modulus of the composites depends on the matrix of the associated materials. In case of EP and VE matrix higher values were registered than at the mixed resin. There is some modulus decrease, which originates from the mixed resins structure. The main reason of this softening is presumably the mentioned entanglement structure of the hybrid resin matrix. The maximal deformations of the composites were on the same level for each investigated material.

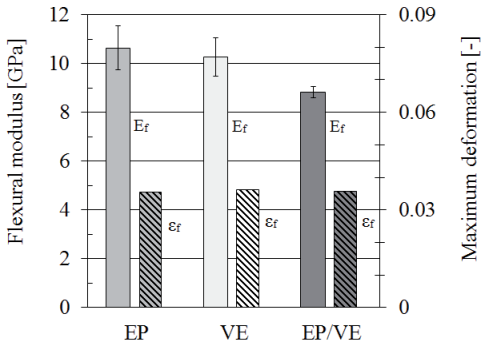

Fig. 5. Flexural modulus (E_f) and max. deformation (ε_f) of the investigated composite materials

From a usability point of view it is important, how a structural material can react on impact loads, therefore Charpy-impact tests were carried out. The composite with EP/VE mixed resin matrix had the highest impact strength among the tested composites (Fig. 6). The reason is the greater energy absorbing property of the IPN matrix. This effect could be manifested in the inter-laminar region of the composite, hence can the flexural- and impact strength be improved, and can the delamination be hampered that is the main damage form in case of such fibre reinforced composites.

Typical load-time curves of the Charpy impact tests are plotted in Fig. 7. They show perfectly the different behaviour of the tested composites. The absorbed energy is the area under the load-time curves. The EP/CF composites showed quite rigid reaction, because after the maximum load the force decreased

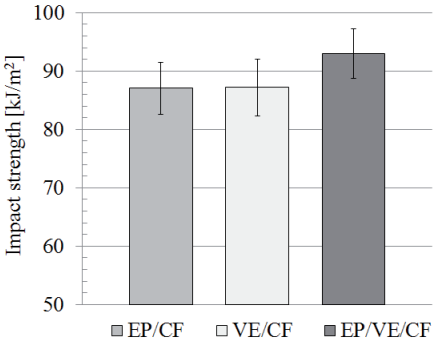

Fig. 6. Impact strength of the composites

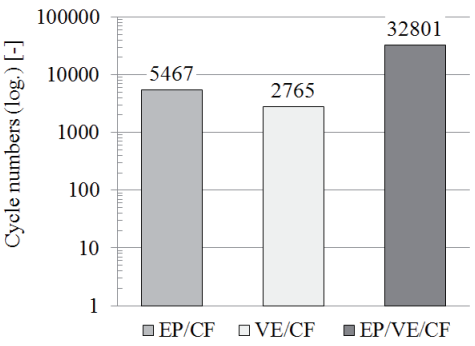

Fig. 8. Abided cycle numbers of composites at flexural fatigue load

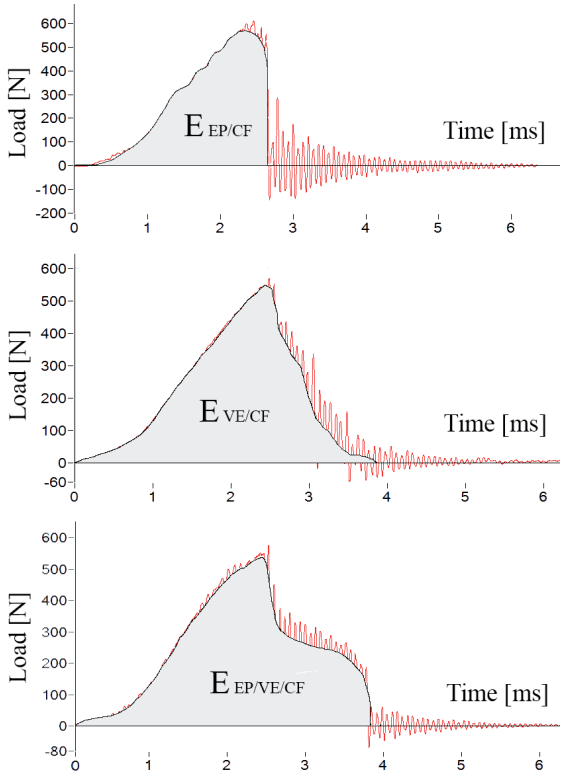

Fig. 7. Load-time curves of Charpy tests of composites

suddenly to zero. The VE/CF composites showed higher damping properties than EP/CF and in this case the fracture was not as rigid as it was in the first case. The best damping properties was reached at the EP/VE/CF composites: their cracking process showed tough behaviour as the load decreased gradually after the maximum force.

The fatigue test is able to model the conditions of the real endurance loads. The results of the flexural fatigue tests showed that the abided cycle numbers of the mixed resin composites (EP/VE/CF) were much higher than, that of the other investigated composites (Fig. 8).

The atomic force microscopy can indicate the low scale structure of the materials. Fig. 9/a and b show the structure of the individual resins. In case of the neat resins nanoheterogeneous structure can be found, this morphology is similar to former published results by other researchers [25, 26] where the structure of EP and VE was detected by AFM. The EP/VE resin has more complex structure (Fig. 9/c) than the individual resins. The mixed resin has specific spatial structure which name is nodular texture. This structure implies the possibility that the resins formed interpenetrating network. The nodular texture was probably created by the stirring method and after that the well dispersed components remained in this morphological position because of the crosslinking. The structure of the composite material (Fig. 9/d) is more detailed than the non-reinforced mixed resin. Probably, the sizing of the carbon fibre could modify the structure during the cross-linking method. The noticed good fatigue properties can be explained by this nanostructure of the EP/VE resin in the composite material. This detailed nanostructured mix has large interphase between its components, that results in better connection. The noticed improvements in the mechanical properties can be explained by this strong connection between the components of the composite and by the numerous entanglements in the matrix.

Conclusions

From the results of the investigations it is visible that the preparation of hybrid resin yielded favourable changes in the mechanical properties of the composites. The thermo-mechanical results showed that the two components (EP and VE) of the mixed resin could work together. The reason of the showed effect can be explained by the entanglements of the molecular chains in the hybrid resin and the detailed nanostructured morphology, which resulted a large sized interphase between the components of the hybrid resin with a lot of secondary bounds. This complex connection between the EP and VE resins lead to the improvement not just in the mechanical properties of the resins but also the mechanical performance of the composites. In cases both of resins and composites nearly to 10% higher flexural strength were showed by the hybrid resin containing ones. For the impact strength up to 7% improvement can be registered at the mixed matrix composites, and these EP/VE resin contained materials bore one order of magnitude higher cycle number of loads in case of fatigue tests. It can be stated

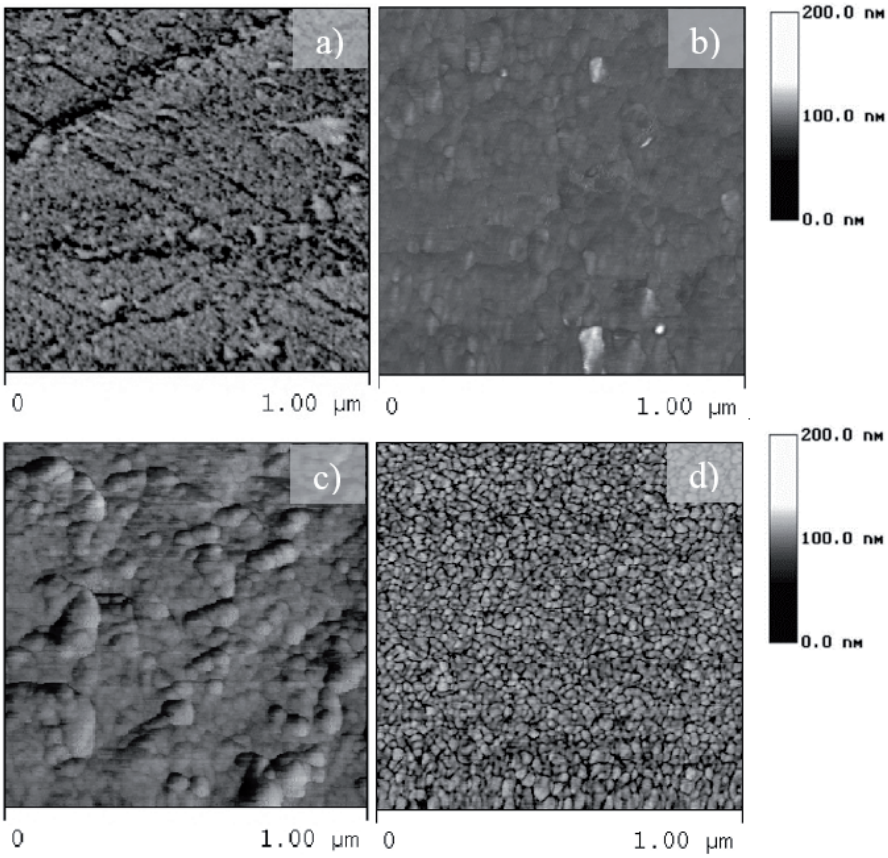

Fig. 9. AFM pictures about the resins VE a), EP b), EP/VE c) and hybrid-composite material EP/VE/CF d)

about the EP/VE matrix composite, that this material showed higher static-mechanical properties, like flexural strength and improved fatigue behaviour than the other neat resin containing ones. On the other hand beyond the mechanical approach there are two important benefits of EP/VE hybrids compared to the individual resins. The first is the reduced styrene content as related to that of the neat VE resin and the second is the reduced cost compared to the initial EP-resin.

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References

1 **Friedrich K., Fakirov S., Zhang Z.,** *Polymer Composites from Nano- to Macro-Scale.* Springer-Verlag, New York, (2005).

2 **Strobl G. R.,** (2007) *Polymer Mixtures: Concepts for understanding their structures and behaviour*. In: The Physics of Polymers. Springer-Verlag, New York, pp. 83-119, (2005). DOI: 10.1007/978-3-540-68411-4

3 **Lipatov Y. S.,** *Phase-separated interpenetrating polymer networks*. Springer-Verlag, Berlin, Heidelberg (2007). DOI: 10.1007/978-3-540-73552-6

4 **Karger-Kocsis J.,** *Simultaneous interpenetrating network structured vinylester/epoxy hybrids and their use in composites*. In: Harrats C., Thomas S., Groeninckx, G. (eds.) *Micro- and Nanostructured Multiphase Polymer Blend Systems: Phase Morphology and Interfaces*. CRC Press; Boca Raton (2005).

5 **Karger-Kocsis J., Gryshchuk O., Jost N.,** *Toughness response of vinylester/epoxy- based thermosets of interpenetrating network structure as a function of the epoxy resin formulation: Effects of the cyclohexylene linkage*. Journal of Applied Polymer Science, 88 (8), pp. 2124-2131, (2003). DOI: 10.1002/app.11946

6 **Park S. J., Jin J. S.,** *Energetic studies on epoxy–polyurethane interpenetrating polymer networks*. Journal of Applied Polymer Science, 82 (3), pp. 775-780, (2001). DOI: 10.1002/app.1903

7 **Chern Y. C., Tseng S. M., Hsiek K. H.,** *Damping properties of interpenetrating polymer networks of polyurethane-modified epoxy and polyurethanes*. Journal of Applied Polymer Science, 74 (2), pp. 328-335, (1999). DOI: 10.1002/(SICI)1097-4628(19991010)74:2<328::AID-APP14>3.0.CO;2-W

8 **Cascaval C. N., Ciobanu C., Rosu D., Rosu L.,** *Polyurethane–epoxy maleate of bisphenol a semi-interpenetrating polymer networks*. Journal of Applied Polymer Science. 83 (1), pp. 138-144, (2002). DOI: 10.1002/app.2236

9 **Hsieh K. H., Han J. L., Yu C. T., Fu S. C.,** *Graft interpenetrating polymer networks of urethane-modified bismaleimide and epoxy (I): mechanical behavior and morphology*. Polymer, 42 (6), pp. 2491-2500, (2001). DOI: 10.1016/S0032-3861(00)00641-8

10 **Meyer G. C., Mehrenberger P. Y.,** *Polyester-polyurethane interpenetrating networks*. European Polymer Journal, 13 (5), pp. 383-386, (1977). DOI: 10.1016/0014-3057(77)90100-8

11 **Hsu T. J., Lee J. L.,** *Processing of polyurethane–polyester interpenetrating polymer network (IPN)*. Journal of Applied Polymer Science, 36 (5). pp. 1157-1176, (1988). DOI: 10.1002/app.1988.070360517

12 **Sands J. M., Jensen R. E., Fink B. K., McKnight S. H.,** *Synthesis and properties of elastomer-modified epoxy–methacrylate sequential interpenetrating networks*. Journal of Applied Polymer Science, 81 (3), pp. 530-545, (2001). DOI: 10.1002/app.1468

13 **Dean K., Cook W. D., Rey L., Galy J., Sautereau H.,** *Near-Infrared and Rheological Investigations of Epoxy−Vinyl Ester Interpenetrating Polymer Networks*. Macromolecules, 34 (19), pp. 6623-6630, (2001). DOI: 10.1021/ma010438z

14 **Dean K., Cook W. D., Zipper M. D., Burchill P.,** *Curing behaviour of IPNs formed from model VERs and epoxy systems I amine cured epoxy*. Polymer, 42 (4), pp. 1345-1359, (2001). DOI: 10.1016/S0032-3861(00)00486-9

15 **Dean K., Cook W. D., Burchill P., Zipper M.,** *Curing behaviour of IPNs formed from model VERs and epoxy systems: Part II. Imidazole-cured epoxy*. Polymer, 42 (8), pp. 3589-3601, (2001). DOI: 10.1016/S0032-3861(00)00745-X

16 **Ivankovic M., Dzodan N., Brnardic I., Mencer H. J.,** *DSC study on simultaneous interpenetrating polymer network formation of epoxy resin and unsaturated polyester*. Journal of Applied Polymer Science, 83 (12), pp. 2689-2698, (2002). DOI: 10.1002/app.10246

17 **Lin M.-S., Liu C.-C., Lee C.-T.,** *Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy*. Journal of Applied Polymer Science, 72 (4), pp. 585-592, (1999). DOI: 10.1002/(SICI)1097-4628(19990425)72:4<585::AID-APP15>3.0.CO;2-M

18 **Szabó J. S., Karger-Kocsis J., Gryshchuk O., Czigány T.,** *Effect of fibre surface treatment on the mechanical response of ceramic fibre mat-reinforced interpenetrating vinylester/epoxy resins*. Composites Science and Technology, 64 (10-11), pp. 1717–1723, (2004). DOI: 10.1016/j.compscitech.2004.01.006

19 **Karger-Kocsis J., Gryshchuk O., Schmitt S.,** *Vinylester/epoxy-based thermosets of interpenetrating network structure: An atomic force microscopic study*. Journal of Materials Science, 38 (3), pp. 413-420, (2003). DOI: 10.1023/A:1021855228253

20 **Gryshchuk O., Karger-Kocsis J.,** *Nanostructure in Hybrid Thermosets with Interpenetrating Networks and its Effect on Properties*. Journal of Nanoscience and Nanotechnology, 6 (2), pp. 345-351, (2006).

21 **Mingkang A., Daofang S., Guojun W.,** *Study on the Structure and Properties of a Hybrid Resins*. International Journal of Chemistry, 1 (2), pp. 10-19, (2009).

22 **Karger-Kocsis J., Castellà N., Grishchuk S.,** *Hybrid resins from polyisocyanate, vinyl ester, melamine formaldehyde and water glass: structure and properties*. Plastics, Rubber and Composites, 37 (5-6), pp. 204-209, (2008). DOI: 10.1179/174328908X309349

23 **Grishchuk S., Karger-Kocsis J.,** *Hybrid thermosets from vinyl ester resin and acrylated epoxidized soybean oil (AESO)*. Express Polymer Letters, 5 (1), pp. 2-11, (2011). DOI: 10.3144/expresspolymlett.2011.2

24 **Venkatanarayanan P. S., Stanley A. J.,** *Intermediate velocity bullet impact response of laminated glass fiber reinforced hybrid (HEP) resin carbon nano composite*. Aerospace Science and Technology, 21 (1), pp. 75-83, (2012). DOI: 10.1016/j.ast.2011.05.007

25 **Grishchuk S,. Bonyár A., Elsäßer J., Wolynski A., Karger-Kocsis J., Wetzel B.,** *Toward reliable morphology assessment of thermosets via physical etching: Vinyl ester resin as an example*. Express Polymer Letters, 7 (5), pp. 407-415, (2013). DOI: 10.3144/expresspolymlett.2013.38

26 **Gu X., Nguyen T., Oudina M., Martin D., Kidah B., Jasmin J., Rezig A., Sung L., Byrd E., Martin J. W., Ho D. L., Jean Y. C.,** *Microstructure and Morphology of Amine-Cured Epoxy Coatings Before and After Outdoor Exposures—An AFM Study*. Journal of Coatings Technology and Research, 2 (7), pp. 547-556, (2005). DOI: 10.1007/s11998-005-0014-x